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EP 0 870 778 A1

(12)

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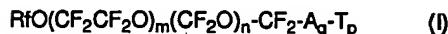
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(54) Modified hydrogenated polymers

(57) Hydrogenated fluoromodified polymers obtainable by reaction among hydrogenated polymers and the modifier having a polyether structure:



wherein A is a linking bridge bound to the end group -CF<sub>2</sub>- of the perfluoropolyether chain, T represents one or more reactive functional groups; p and q are integers, p ranges from 1 to 4, q is an integer from 0 to 1; m and n are integers such that m/n is comprised between 0.2 and 5, Rf is a perfluoroalkyl from 1 to 3 carbon atoms.

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**Description**

5 The present invention relates to hydrogenated modified polymers with perfluoropolyethers, said polymers can have linear or cured structure, and can be used both as films and as manufactured articles, characterized by improved surface properties with respect both to the corresponding hydrogenated polymers and to the same modified polymers with the fluorinated macromers of the prior art.

10 More particularly the present invention relates to polymers having an extremely selective enrichment of the fluorinated modifier at the surface which gives an improved hydro/oil-phobicity of the same and specifically an higher contact angle and a lower friction coefficient.

15 It is known in the art to modify hydrogenated polymeric structures by the use of fluorinated derivatives, in particular having a perfluoropolyether structure, to give good surface properties.

20 However there was a need to have available extremely effective modifiers allowing, the concentration of the fluorinated modifier being equal, to obtain a higher contact angle and a lower friction coefficient, since, for instance, in the dynamic sealing systems, in particular for hydraulic fluids, the optimal combination of these two properties allows to guarantee an optimal gasket sealing in the time by reducing abrasion and chemical attack phenomena of the same due to the service fluid.

25 Another example showing a need to have available said modifiers resides in the coating field where the low film thickness often results in an insufficient resistance to the chemical attack due to solvents or aggressive agents generally used as detergents or present in the chemical industry sectors where these films are used as anticorrosion coatings.

30 At the same time it is also required that the film has a low friction coefficient to reduce the surface abrasion phenomena which determine a lowering of the gloss properties (gloss decrease) and of the imagine definition (D.O.I.) of the films.

35 It has been unexpectedly and surprisingly found a perfluoropolyether structure modifier able to react by chemically binding to the hydrogenated polymeric structure avoiding undesired release phenomena, in the time, of fluorinated not chemically bound species. In fact the perfluoropolyethers with non reactive end groups, due to the the lack of reactive functional groups, besides not assuring a constancy of the performances in the time, would not be acceptable in applications where release phenomena would cause pollutions of the system in which the film or the polymer is used or absorptions due to biological tissues with non checkable and potentially dangerous effects.

40 An object of the present invention are hydrogenated fluoromodified polymers obtainable by polycondensation or polyaddition reaction or by grafting among hydrogenated monomeric, oligomeric or polymeric species with the following modifier having a polyether structure:



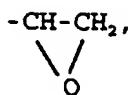
45 wherein A is a linking bridge bound to the end group  $-CF_2-$  of the perfluoropolyether chain, T represents one or more reactive functional groups; p and q are integers, p ranges from 1 to 4, preferably from 1 to 2, q is an integer equal to 0 or 1; m and n are integers such that m/n is comprised between 0.2 and 5, preferably between 1 and 4, m and n are preferably such that the number average molecular weight is comprised between 400 and 5000, preferably between 600 and 2000; Rf is a perfluoroalkyl from 1 to 3 carbon atoms, optionally containing 1 chlorine and/or hydrogen atom.

50 The linking bridge A is a bivalent radical between the perfluoromethylene group of the fluorinated chain and the T reactive end groups. Preferably it is of linear aliphatic type as  $-(CH_2)_{m'}-$  wherein m' is an integer from 1 to 20; of (alkylen)cycloaliphatic or (alkylen)aromatic type wherein the alkylen has 1 to 20 C atoms, A optionally can contain heteroatoms in the ring or in the alkylene chain, for example N, P, S, O; it can be a polyalkylenoxy, both linear and branched, chain in particular containing repeating units of the type  $-CH_2CH_2O-$ ,  $-CH_2CH(CH_3)O-$ ,  $-(CH_2)_3O-$ ,  $-(CH_2)_4O-$ . The linking bridge A can also contain groups of amidic, ester, ether, COO, sulphur, imine type. A can also be a combination of the indicated types. The number of carbon atoms of the cycloaliphatic compounds being from 3 to 20, for the aromatic ones from 5 to 20.

55 A can be for instance:  $-O-$ ,  $-CR_aR_b-$ ,  $-CONR-$  wherein R<sub>a</sub> and R<sub>b</sub> equal or different from each other are equal to R; and R is H, alkylic, cycloaliphatic or aromatic groups, all having less than 15 carbon atoms, preferably H or alkylic,  $-COO-$ ,  $-COS-$ ,  $-CO-$ , an heteroatom, or triazinic, heterocyclic aromatic groups with 5 or 6 atoms containing 2 or more heteroatoms equal to or different from each other, for example N, P, S, O.

60 T is an end group able to render mono, bi- or polyfunctional the structure, such as to make it reactive towards co-reactants or substrates. The substrates can be both natural and synthetic: paper, cotton, wood, stony materials, polymeric materials, metal or inorganic substrates can be mentioned.

65 In particular T can be for instance:  $-OH$ ,  $-SH$ ,  $-SR'$ ,  $-NR'_2$ ,  $-COOH$ ,  $-SiR'_4$ ,  $Q_{3-4}$ ,  $-CN$ ,  $-NCO$ ,  $-CH=CH_2$ .



10 -COR', -OSO<sub>2</sub>CF<sub>3</sub>, -OCOCl, -OCN, -N(R')CN, -(O)COC(O)-, -I, -CHO, -CO, -CH(OCH<sub>3</sub>)<sub>2</sub>, -SO<sub>2</sub>Cl, -C(OCH<sub>3</sub>)=NH, -C(NH<sub>2</sub>)=NH, -CH(OH)CH<sub>2</sub>OH, -CH(COOH)<sub>2</sub>, -CH(COOR')<sub>2</sub>, -CH(CH<sub>2</sub>OH)<sub>2</sub>, -CH(CH<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>, -CH(CN)<sub>2</sub>, -CH(CH<sub>2</sub>OCH<sub>2</sub>CH=CH<sub>2</sub>)<sub>2</sub>, wherein R' is an alkylic having from 1 to 20 C atoms, (alkyl)cycloaliphatic or (alkyl)aromatic group having preferably from 5 to 20 C atoms, R' optionally containing fluorine, Q is an -O(CO)<sub>d0</sub>R' group, d is an integer comprised between 0 and 3, d<sub>0</sub> is 0 or 1.

15 The compounds of formula (I) are prepared, for instance, from acids, esters or from acyclic halides of poly(perfluoroalkylenoxides) by known reactions, for instance, according to what indicated in Table I.

15

	-A-T of formula (I)	Reactant
20	1 -CONHCH <sub>2</sub> -CH=CH <sub>2</sub>	H <sub>2</sub> NCH <sub>2</sub> -CH=CH <sub>2</sub>
	2 -CONH(CH <sub>2</sub> ) <sub>3</sub> CO <sub>2</sub> H	H <sub>2</sub> N(CH <sub>2</sub> ) <sub>3</sub> CO <sub>2</sub> H
25	3 -CON(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>2</sub> OH	HN(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>2</sub> OH
	4 -CONHCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>
30	5 -CONHCH <sub>2</sub> CH <sub>2</sub> SH	H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> SH
	6 -CONH(CH <sub>2</sub> ) <sub>3</sub> Si(OCH <sub>3</sub> ) <sub>3</sub>	H <sub>2</sub> N(CH <sub>2</sub> ) <sub>3</sub> Si(OCH <sub>3</sub> ) <sub>3</sub>

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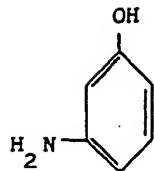
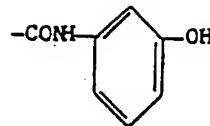
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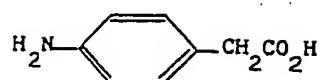
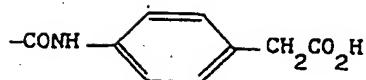
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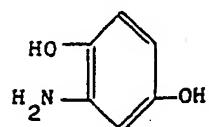
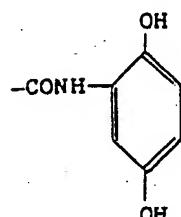
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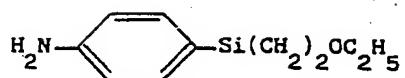
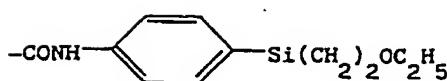
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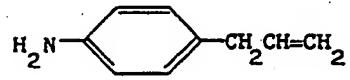
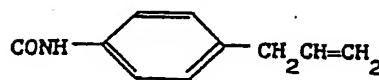
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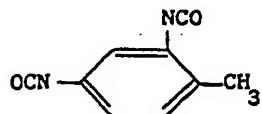
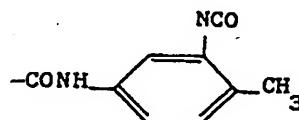
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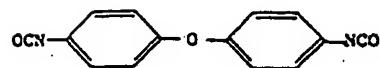
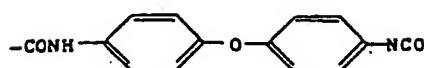
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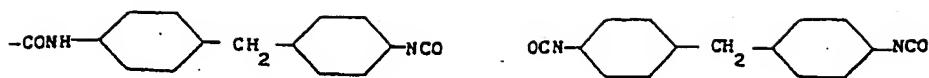
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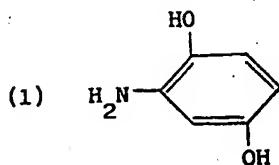
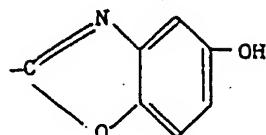
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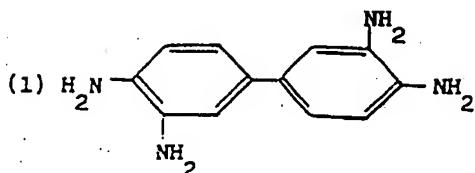
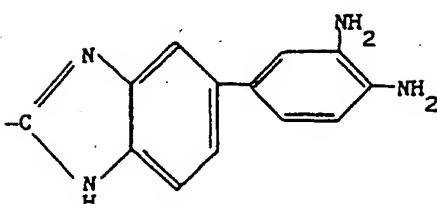
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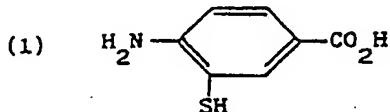
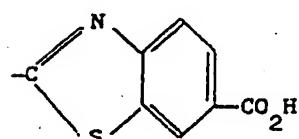
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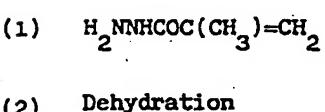
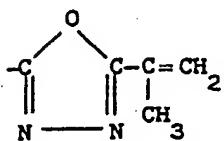
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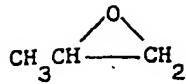
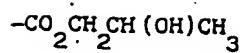


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19 -CO<sub>2</sub>CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>OHHOCH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>OH

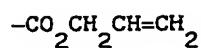
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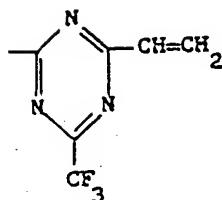
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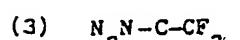
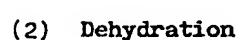
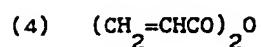
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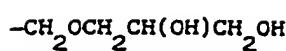
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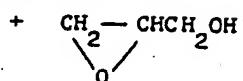


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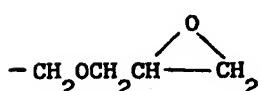


Compound 24



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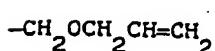
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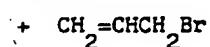
Compound 24 + epibromidrine

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Compound 24



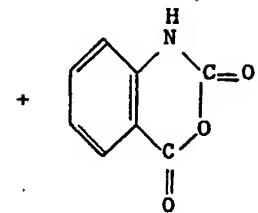
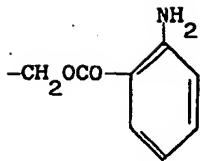
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Compound 24

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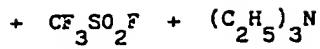
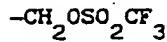
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Compound 24

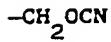


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Compound 24

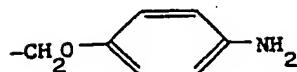
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(1) Compound 29



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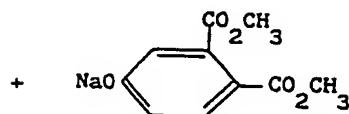
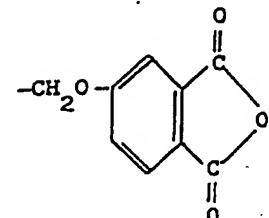
Compound 31 + phosgene

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33

(1) Compound 29

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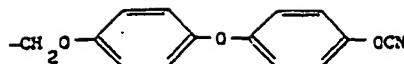
(2) Hydrolysis

(3) Acetic anhydride

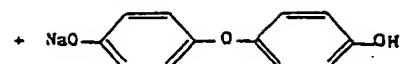
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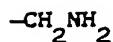
(1) Compound 29



(2) ClCN + triethylamine

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Compound 29 + NH<sub>3</sub>

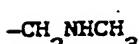
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Compound 35 + COCl<sub>2</sub>

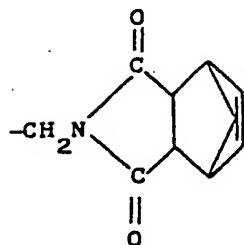
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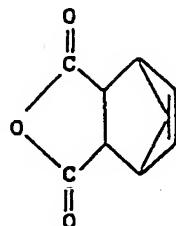
Compound 29 + CH<sub>3</sub>NH<sub>2</sub>

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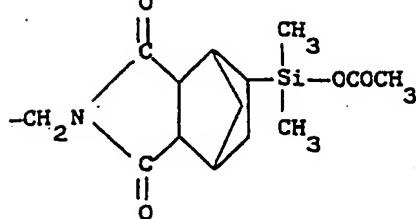
Compound 35 +



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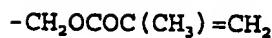
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Compound 38 + HSi(CH<sub>3</sub>)<sub>2</sub>OCOCH<sub>3</sub> + H<sub>2</sub>PtCl<sub>6</sub>

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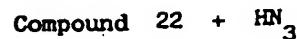
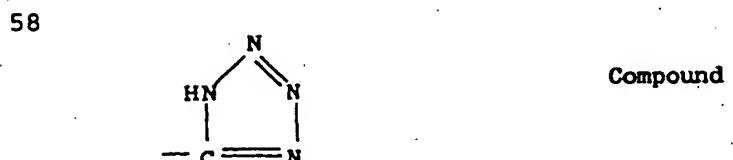
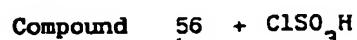
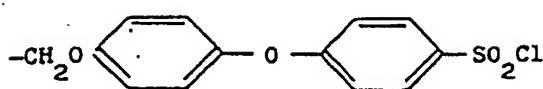
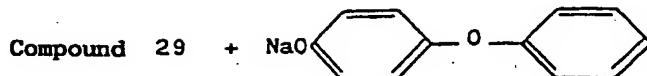
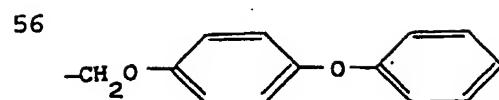
50

40

Compound 24 + CH<sub>2</sub>=C(CH<sub>3</sub>)COCl

55

41	$-\text{CH}_2\text{I}$	Compound 29 + NaI	
5			
42	$-\text{CH}_2\text{SH}$	(1) Compound 29+ $\text{CH}_3\text{COSNa}$ (2) Hydrolysis	
10			
43	$-\text{CH}_2\text{N}^+\equiv\text{C}^-$	(1) Compound 35+ $\text{HCO}_2\text{CH}_3$ (2) $\text{COCl}_2+(\text{C}_2\text{H}_5)_3\text{N}$	
15			
20	44	$-\text{NCO}$	(1) $\text{NaN}_2$ (2) Heating
25	45	$-\text{COC}_6\text{H}_5$	$\text{Cd}(\text{C}_6\text{H}_5)_2$
30	46	$-\text{C}(\text{CH}_3)_2\text{OH}$	(1) $\text{CH}_3\text{MgBr}$ (2) $\text{H}^+$
35	47	$-\text{CHO}$	$\text{LiAlH}_4$
40	48	$-\text{C}(\text{CH}_3)=\text{CH}_2$	Compound 46+ $\text{P}_2\text{O}_5$
45	49	$-\text{CH}_2\text{N}(\text{CN})\text{CH}_3$	Compound 37+ $\text{ClCN}+(\text{C}_2\text{H}_5)_3\text{N}$
50	50	$-\text{I}$	(1) $\text{Ag}_2\text{O}$ (2) $\text{I}_2$
55			

51  $-\text{CH}=\text{CH}_2$  Compound 47 +  $\text{CH}_2=\text{P}(\text{C}_6\text{H}_5)_3$ 52  $-\text{C}(\text{OCH}_3)=\text{NH}$  Compound 22 +  $\text{CH}_3\text{OH} + (\text{C}_2\text{H}_5)_3\text{N}$ 10 53  $-\text{CH}_2-\text{SO}_2\text{Cl}$  Compound 42 +  $\text{Cl}_2 + \text{H}_2\text{O}$ 15 54  $-\text{CH}(\text{OCH}_3)_2$  Compound 47 +  $\text{CH}_3\text{OH} + \text{acido}$ 20 55  $-\text{C}(\text{NH}_2)=\text{NH}$  Compound 22 +  $\text{NH}_3$ 

55 The fluorinated modifiers of the invention are generally used from 100 ppm to 10% by weight, these not being absolute but only indicative limits and the skilled will choose then the optimal amount to obtain the performances indicated above combined with the specific properties of the single base hydroogenated polymers.

A further object of the present invention is represented by both the modifiers as such and the process for obtaining them.

The Applicant has indeed surprisingly found a process which allows to prepare the modifiers of the invention in an extremely selective way and with an high yield.

5 The preparation process of the modifiers of the invention of formula (I) comprises the following steps:

- synthesis of the raw peroxidic material by reaction of tetrafluoroethylene with oxygen in absence of UV radiations and in the preence of radical initiators;
- reduction of the raw peroxidic material to obtain perfluoropolyethers free from peroxidic groups and containing 10 chains with -COF end groups and such that the functionality of the obtained product is lower than 1.8;
- esterification of the -COF groups by reaction with alcohols to obtain the -COOR' end groups;
- chemical reduction of the esters to alcohols -CH<sub>2</sub>OH;
- separation of the monofunctional species -CH<sub>2</sub>OH from the reaction mixture by an adsorption/de-adsorption process on stationary phases;
- 15 - optional transformation of the -CH<sub>2</sub>OH end groups in other functional groups to obtain -A-T of formula (I).

The process comprises the preparation of peroxidic perfluoropolyethers, the end groups of the perfluoropolyether can contain 1 chlorine and/or hydrogen atom, by reacting tetrafluoroethylene with oxygen in liquid phase at temperatures lower than 50°C and in the presence of one or more initiators having 1 or more F-X<sub>1</sub> bonds, wherein X<sub>1</sub> is selected 20 from fluorine, oxygen and chlorine, the compounds having the F-O bond are selected from the organic compounds containing 1 or more fluoroxy groups. This first reaction step is described in USP 5,228,110 herein incorporated by reference.

The raw peroxidic perfluoropolyethers are subjected to a reduction treatment to eliminate the peroxidic bonds transforming them into functional groups -COF. This reaction step is carried out for instance by utilizing the processes 25 described in USP 3,847,978 herein incorporated by reference. In particular the reduction is carried out with hydrogen in the presence of a palladium catalyst on a carbon support, the amount of palladium being about 1% based on the support.

The raw peroxidic material obtained in the first reaction step must be such as to bring to products having -COF functionality lower than 1.8, preferably lower than or equal to 1.55, to obtain high yields in pure monofunctional product.

30 The acyclic fluorides thus obtained are esterified with hydrogenated or fluorinated alcohols, for instance according to USP 3,847,978. Specifically a direct esterification is carried out with alcohols from 1 to 6 carbon atoms. The obtained product with functionality COOR', wherein R' is the alkylic part of the used alcohol, has an average functionality almost corresponding to that of the previous acyclic derivative before esterification.

The subsequent ester reduction step to obtain the corresponding alcohol is preferably carried out with sodiumborohydride. The obtained alcoholic functionality is about the one corresponding to the above acyclic fluoride.

The product thus obtained is then subjected to a separation/purification process based on the selective adsorption/de-adsorption of the monofunctional species present in the mixture by using stationary phases able to have a different bond strength with the species having a different alcoholic functionality present in the mixture. The separation process is preferably carried out according to USP 5,262,057, herein incorporated by reference, or according to the Italian Patent MI96A001672 in the name of the Applicant. Specifically it is used, as stationary phase, silica in a chromatographic column and subsequent elution processes with solvents having eluotropic progressively increasing strength, or in a batch process with stirred reactor and subsequent filtration. The chromatographic separation process is preferably carried out by using silica, previously washed with methanol, dried at 150°C. The mixture of perfluoropolyethers having 40 alcoholic functionality is passed through the column, optionally the mixture is diluted with the non polar eluent itself, and it is eluted with non polar solvents characterized by an eluotropic strength epsilon lower than 0.05 referred to the silica, preferably selected from trichlorotrifluoroethane, perfluoropolyethers having low molecular weight and low viscosity lacking of functional groups, perfluoroalkanes mono- and dihydroperfluoropolyethers with low molecular weight and low viscosity, hydrochlorofluorocarbons H(C)FC, fluoroaromatics selected from trifluorotoluene, bis-trifluoromethylbenzene isomers, perfluorobenzene. The first eluted fraction is formed by all the perfluoropolyethers lacking of alcoholic functional groups and by smaller amounts of monofunctional products. The subsequent fractions only contain the monofunctional products wherein the functionality generally ranges between 0.97 and 1.03, preferably 0.98 and 1.02. Generally, if a product having an average functionality 1.5 in acyclic fluoride is considered, the first fraction is lower than 5% by weight, the useful subsequent fractions are about the 40-50% by weight based on the raw alcoholic mixture.

45 The monofunctional product -CH<sub>2</sub>OH is then, optionally, transformed according to the above reactions to obtain other functional groups -A-T of formula (I) suitable to react with the various hydrogenated co-reactants, hydrogenated polymers containing reactive functional groups to give the modified polymers of the invention. In the case of substrates, natural or synthetic, depending on the reactive group of the substrate the above reaction can takke place. When the substrate has no reactive groups towards T of the modifier, the modifier is adsorbed on the surface through hydrogen

bonds or Van der Waal forces. In this case this phenomenon is indicated in this application as adsorption of the modifier on the surface.

For illustrative purpose two classes of polymeric materials have been selected: polyurethanes and polyacrylates belonging respectively to the thermoprocessable elastomers and to the cured films family, to show the advantages obtainable with the modifiers of the invention compared with the corresponding non modified polymeric materials or modified with fluorinated bifunctional or monofunctional modifiers of the art. Unexpectedly it was found that the modification with the derivatives of formula (I) of the present invention not only shows advantages with respect to the non modified polymer but also with respect to the monofunctional perfluoropolyethers known in the art having a similar structure and also with respect to the products having the same sequences of the modifiers of formula (I) but containing two functional groups on both chain end groups (Rf of formula (I) is equal to the functional group -A-T). This property combination - lower friction coefficient and high contact angles - allows to obtain improved surface properties as it is requested in the above application fields.

The obtainment of the hydrogenated fluoromodified polymers of the present invention can be achieved by means of processes well known in the art, such as, for instance, polycondensation, polyaddition, grafting reactions.

The following examples are given for illustrative but not limitative purposes of the present invention.

EXAMPLE 1: Preparation of the raw material having alcoholic functionality

EXAMPLE 1A: Preparation of the peroxidic perfluoropolyether

Example 6 of USP 5,258,210 was repeated but using an amount of  $CF_3OF$  (Ni/h of 0.25) obtaining a raw peroxidic material characterized by:

a) number average molecular weight (PM) 3700, and oxidizing power (PO) 2.94.

Example 7 of USP 5,258,210 was repeated using an initiator F amount of 0.18 Ni/h and using a TFE amount of 1 Ni and an oxygen amount of 5 Ni/h obtaining a product having the following characteristics:

b) number average molecular weight (PM) 1620, and oxidizing power (PO) 1.27.

EXAMPLE 1B: Catalytic hydrogenation

Catalytic reduction of the raw peroxidic materials a) and b) of Example 1A is carried out by means of Example 10 of USP 3,847,978 to obtain acid fluoride (the subsequent hydrolysis treatment with 40% sulphuric acid is not carried out).

The following acid fluorides are respectively obtained:

a) PM 720 (equivalent weight PE 470); average functionality: 1.53  
 b) PM 709 (equivalent weight PE 627); average functionality: 1.13

EXAMPLE 1C: Esterification

The acid fluorides a) and b) of Example 1B are transformed into the respective methyl esters by reaction at room temperature with methanol and elimination of the developed HF by stripping at 70°C by nitrogen stream. The following methylic esters are obtained (as widely described in the art, for instance also in the previous Patent):

a) PM 737 (PE 485) average functionality: 1.52  
 b) PM 730 (PE 658) average functionality: 1.11

EXAMPLE 1D: Reduction with  $NaBH_4$

The products obtained in Example 1C are subjected to reduction with  $NaBH_4$  in ethanol and subsequent acid hydrolysis of the intermediate boric esters allowing to obtain the corresponding alcoholic derivatives:

a) PM 811 (PE 539) average functionality: 1.50  
 b) PM 800 (PE 728) average functionality: 1.10

EXAMPLE 1E: Chromatographic purification

5 The product obtained in Example 1D was separated by chromatography by using a silica column (3.3 Kg), 1 Kg of ZDOL having an average functionality of 1.50 (product a) of Example 1D), and limiting the pretreatment of the column only to the washing with CFC-113. The elution is carried out with the use of only the solvent with low polarity CFC-113 to separate the neutral and monofunctional fractions.

In particular a first elution with 85 l of CFC-113 and a subsequent elution with 43 l of a mixture of CFC-113/methanol (9/1) allow to collect the following fractions (of which also the NMR analysis is reported):

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Fraction	Eluent	Amount (g)	MW	EW	Aver. Funct.
1.	113	35	1810	6530	0.23
2.	113	107	1309	1330	0.98
3.	113	316	924	892	1.02
4.	113/CH <sub>3</sub> OH	497	699	370	1.88

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EXAMPLE 2: Synthesis of the carboxylic monoacid

25 In a 250 ml glass flask equipped with condenser, mechanical stirrer and thermometer, containing a solution of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O (16.6 g, 35.5 g and 25.4 g respectively), maintained at 80°C, 50 g of Z monoalcohol are added in 1 hour, obtained according to the previous Example, (fraction 3, EW 892, equal to 56 meq).

The reaction mass is maintained at 80°C for 4 hours, then is poured into 2.5 l of water. 2 extractions with 500 ml each of H-GALDEN are carried out. The aqueous phase is treated with 500 ml of isopropanol and then extracted with 500 ml of H-GALDEN.

30 The solutions containing H-GALDEN are put together, treated with sodium sulphate, filtered and the solvent evaporated.

47 g of product are recovered which at the N.M.R. and I.R. analyses result to be the corresponding carboxylic monoacid (yield 95%).

EXAMPLE 3: Synthesis of the methyl monoester

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In a 250 ml glass flask equipped with condenser, thermometer and mechanical stirrer, 40 g of carboxylic monoacid (acid equivalent weight 910, equal to 44 meq acid) prepared according to the previous Example, are introduced.

100 ml of anhydrous methanol containing 1 g of dissolved HCl are added. Then the reaction mass is reflux heated, then it is let under reflux for three hours, it is cooled at room temperature and the upper methanol phase is separated, 40 then the methanol dissolved in the product is removed by distillation and 40 g of product are separated which at the NMR and IR analyses result to be the corresponding methyl ester.

EXAMPLE 4: Functionalization of the Z monoalcohol derivative to obtain the corresponding diolic derivative (the two OH end groups are on the same group A)

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With the purpose to obtain a bifunctional derivative, i.e. suitable to be used as reactive additive for polymeric materials and lacking of undesired effects typical of a monofunctional reactive additive (for instance the termination of the growing polymeric chain), 15 g of mono-ol Z fraction 3 (partially saponified with K-terbutylate, 5%) are reacted with glycidol in terbutanol at 80°C (according to what is described in the literature, for instance in Die Angewandte Makromolekulare Chemie, 231, 47 (1995)). A diolic derivative having a PFPE chain and the two reactive groups on the same chain end group is thus obtained; this allows to obtain a reactive additive able to give chain-extension (without therefore reducing the length of the growing molecular chain) and to have however a free PFPE part:



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wherein the m and n indexes are integers such as to give a number average molecular weight of the fluorinated chain of 860, and the m/n ratio is 2.

EXAMPLE 5: Synthesis of Z-urethan-methacrylate

The mono-ol Z (fraction 3) is reacted with ethylisocyanate methacrylate (EIM) in CFC-113 containing some drops of DBTDL as catalyst, the reaction is completed at 50°C in 8 hours.

A macromeric derivative having a segmented structure is thus obtained which consists of one part containing PFPE sequences and of another methacrylic hydrogenated part (suitable therefore for a subsequent UV or peroxidic curing with unsaturated hydrogenated reactants):

EXAMPLE 6 (comparative)

Example 1 was repeated to obtain a perfluoropolyether monoalcohol having a mono Y structure:



wherein the r, t indexes are integers such as to give a number average molecular weight of 800, the r/t ratio is 40, Rf has the above meaning, using perfluoropropene instead of tetrafluoroethylene in Example 1A.

The corresponding diol was then prepared according to the procedure indicated in Example 4.

EXAMPLE 7 (comparative): a1) reference hydrogenated PU

According to the details described in EP 621,298 an hydrogenated polyurethane polymer is prepared by means of a two steps process which includes in a first phase the synthesis of the NCO ended prepolymer and in a subsequent phase the chain-extension and press polymerization, starting from:

30	polycaprolactone diol methylenediphenylenediisocyanate hydroquinoneethoxylate	(PCL) (MDI) (HQE)	1 eq. 2.5 eq. 1.5 eq.
----	-------------------------------------------------------------------------------------	-------------------------	-----------------------------

EXAMPLE 8: b1) PU additized with Z diol (from monoalcohol) of Example 1

To the NCO ended prepolymer synthetized as in the previous Example the derivative obtained by reaction between the mono Z and the glycidol (1% w/w based on the total amount), obtained according to Example 4, is added.

It is allowed to react for 1 hour at 90°C and then the chain-extension with HQE and the polymerization are completed as in the previous case.

EXAMPLE 9 (comparative): c1) PU additized with Y diol (from monoalcohol) according to Example 6

To the NCO ended prepolymer synthetized as in the previous Example the derivative obtained by reaction between the mono Y and the glycidol (1% w/w based on the total amount), obtained according to the details described in Example 6, is added.

It is allowed to react for 1 hour at 90°C and then the chain-extension with HQE and the polymerization are completed as in the previous case.

On the three polymeric materials thus synthetized, the hardness, the friction coefficient and the surface energy by contact angles were determined, the results can be summarized as follows:

Table 1

Material	Hardness Shore A	Friction coeff.		Surface energy mN/m
		2.01N	7.01N	
a1)(cfr.)	87	0.63	0.46	30.05

Table 1 (continued)

Material	Hardness Shore A	Friction coeff.		Surface energy mN/m
		2.01N	7.01N	
b1)	87	0.35	0.24	16.3
c1)(cfr.)	87	1.60	1.35	17.4

## EXAMPLE 10: Preparation of cured films

Mixtures containing bisphenol A-dihydroxyethylacrylate and variable amounts of Z urethanmethacrylate (0-1% w/w) are deposited on a glass plate and cured by UV radiation in the presence of a photo-initiator (e.g. 2,2-dimethoxy-2-phenylacetophenone) under nitrogen atmosphere.

On the so obtained films the advancing contact angle is determined with bidistilled water, the results can thus be summarized and compared with those of similar films obtained from Z bis-urethanmethacrylate additives synthetized starting from fluorinated diols having a different number average molecular weight (1000 and 2000).

Contact angle measurements were performed with a Kruss G1 instrument and with a Chan balance, DCA 322.

The measurements with the Wilhelmy plate method were made in air at room temperature (20°C) according to that reported in Journal of Colloid and Interface Science 172,48-55 (1995) A. Mennella and N.R. Morrow.

On every sample at least 6 measurements were performed; the difference from the average value was no more than 2° for the advancing angle.

Table 2

Composition % PFPE w/w	Mono Z		Bis Z-1000		Bis Z-2000	
	advancing contact angle with H <sub>2</sub> O					
	air	glass	air	glass	air	glass
0	70	65	70	65	70	65
0.01	78	55	77	70	76	72
0.05	120	56	98	68	85	77
0.10	127	62	104	69	94	81
0.40	124	62	104	70	98	84
0.80	126	75	105	70	100	85
100.00	/	/	124	106	127	112

From analysis data reported in Table 2 it is evident how films obtained with mono Z, for any concentration value of the fluorinated modifier, always give the highest values of the advancing contact angle (air side). Besides these highest values are achieved even at very low concentrations (0.05%); this confirms the greater efficacy of mono Z in giving hydro/oil-phobicity to the film surface with respect to the other comparison PFPE modifiers.

## Claims

1. Hydrogenated fluoromodified polymers obtainable by polycondensation or polyaddition or grafting reaction among hydrogenated monomeric, oligomeric or polymeric species, with the following modifier having a polyether structure:



wherein A is a linking bridge bound to the end group -CF<sub>2</sub>- of the perfluoropolyether chain, T represents one or more reactive functional groups; p and q are integers, p ranges from 1 to 4, preferably 1 or 2, q is an integer 0 or 1; m and n are integers such that m/n is comprised between 0.2 and 5, preferably between 1 and 4, m and n are preferably such that the number average molecular weight is comprised between 400 and 5000, preferably between 600 and 2000; Rf is a perfluoroalkyl from 1 to 3 carbon atoms, optionally containing 1 chlorine and/or hydrogen

atom.

2. Hydrogenated fluoromodified polymers according to claim 1 wherein the linking bridge A is a linking bivalent radical between the perfluoromethylene group of the fluorinated chain and the reactive end groups T, preferably of linear aliphatic type as  $-(CH_2)_m-$  wherein m' is an integer from 1 to 20; of (alkylen)cycloaliphatic, (alkylen)aromatic, A optionally can contain heteroatoms in the ring or in the alkylene chain, preferably the heteroatoms being N, P, S, O, it can be a polyalkylenoxy both linear and branched chain, specifically containing repeating units of the type  $-CH_2CH_2O-$ ,  $-CH_2CH(CH_3)O-$ ,  $-(CH_2)_3O-$ ,  $-(CH_2)_4O-$ , the linking bridge A optionally containing groups of amidic, ester, ether, COO, sulphur, imine type, the number of carbon atoms of the cycloaliphatic compounds being from 3 to 20, for the aromatic ones from 5 to 20; the group A can also be a combination of the indicated types.

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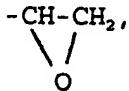
3. Hydrogenated fluoromodified polymers according to claims 1-2 wherein the bond group of A with the perfluoromethylene group of the fluorinated chain is selected from  $-O-$ ,  $-CR_aR_b-$ ,  $-CONR-$ , wherein  $R_a$  and  $R_b$  equal or different from each other are equal to R (R being H, alkylic, cycloaliphatic or aromatic groups having less than 15 carbon atoms),  $-COO-$ ,  $-COS-$ ,  $-CO-$ , an heteroatom, triazinic, heterocyclic aromatic groups with 5 or 6 atoms containing 2 or more heteroatoms equal to or different from each other.

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4. Hydrogenated fluoromodified polymers according to claims 1-3 wherein T is an end group able to render mono, bi- or polyfunctional the structure, such as to make it reactive towards co-reactants or however on substrates.

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5. Hydrogenated fluoromodified polymers according to claim 4, wherein T is selected from:  $-OH$ ,  $-SH$ ,  $-SR'$ ,  $-NR'_2$ ,  $-COOH$ ,  $-SiR'_dQ_3-d-$ ,  $-CN$ ,  $-NCO$ ,  $-CH=CH_2$ ,  $-COR'$ ,  $-OSO_2CF_3$ ,  $-OCOCl$ ,  $-OCN$ ,



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$-N(R')CN$ ,  $-(O)COC(O)-$ ,  $-I$ ,  $-CHO$ ,  $-CO$ ,  $-CH(OCH_3)_2$ ,  $-SO_2Cl$ ,  $-C(OCH_3)=NH$ ,  $-C(NH_2)=NH$ ,  $-CH(OH)CH_2OH$ ,  $-CH(COOH)_2$ ,  $-CH(COOR')_2$ ,  $-CH(CH_2OH)_2$ ,  $-CH(CH_2NH_2)_2$ ,  $-CH(CN)_2$ ,  $-CH(CH_2OCH_2CH=CH_2)_2$ , wherein R' is an alkylic, cycloaliphatic or aromatic group, R' optionally containing fluorine, Q is an  $-O(CO)_{d_0}R'$  wherein  $d_0$  is 0 or 1; d is an integer comprised between 0 and 3.

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6. Hydrogenated fluoromodified polymers according to claims 1-5 wherein the fluorinated modifiers are used from 100 ppm to 10% by weight, based on to the hydrogenated polymer or on the substrate.

7. Modifiers of formula (I) according to claims 1-6.

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8. Process for preparing modifiers of formula (I) according to claim 7 comprising the following steps:

- synthesis of the raw peroxidic material by reaction of tetrafluoroethylene and oxygen in absence of UV radiations and in the presence of radical initiators;
- reduction of the raw peroxidic material to obtain perfluoropolyethers lacking of peroxidic groups and containing chains with end groups  $-COF$  and such that the functionality of the obtained product is lower than 1.8;

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- esterification of the  $-COF$  groups by reaction with alcohols to obtain the end groups  $-COOR'$ ;
- chemical reduction of the esters with alcohols  $-CH_2OH$ ;
- separation of the monofunctional species  $-CH_2OH$  from the reaction mixture by an adsorption/de-adsorption process on stationary phases;

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- optional transformation of the end groups  $-CH_2OH$  into other functional groups to obtain  $-A-T$  of formula (I).

9. Process according to claim 8 wherein the peroxidic perfluoropolyether, the end groups of the perfluoropolyether can contain 1 chlorine and/or hydrogen atom, is obtained by reacting tetrafluoroethylene with oxygen in liquid phase at temperatures lower than 50°C and in the presence of one or more initiators having 1 or more  $F-X_1$  bonds, wherein  $X_1$  is selected from fluorine, oxygen and chlorine.

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10. Process according to claim 9 wherein the compounds having the F-O bond are selected from the organic compounds containing 1 or more fluoroxy groups.

11. Process according to claims 8-10 wherein the separation of the monofunctional species is carried out by a chromatographic separation process wherein as stationary phase silica is used in a chromatographic column and subsequent elution processes with solvents having a progressively increasing elutropic strength.
- 5 12. Process according to claims 8-10, wherein the separation of the monofunctional species is carried out in a batch process with stirred reactor and subsequent filtration.
13. Manufactured articles obtainable by treatment of a natural or synthetic substrate with the modifier according to claim 7.
- 10 14. Manufactured articles according to claim 13 wherein the substrate contains chemically reactive groups towards the T-end groups of the modifier.
15. Manufactured articles according to claims 13-14 wherein the modifier is absorbed on the substrate surface.
16. Use of the modifiers according to claim 7 to prepare hydrogenated fluoromodified polymers according to claims 1-6.
- 20 17. Use of hydrogenated fluoromodified polymers according to claims 1-6 for hydraulic sealing systems.

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European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number

EP 98 10 6099

DOCUMENTS CONSIDERED TO BE RELEVANT									
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)						
X	WO 92 12199 A (MINNESOTA MINING AND MANUFACTURING COMPANY) 23 July 1992 * page 1, line 6 - line 14 * * page 2, line 1 - line 17 * * page 5, line 7 - line 35 * * page 7, line 28 - page 8, line 12; claims 1,4,6-22; examples 28,30,34 * ---	1-7,16, 17	C08F8/18 C08F220/24 C08F220/36 C08G65/00						
A	EP 0 322 916 A (AUSIMONT S.R.L.) 5 July 1989 * claims 1-9 *	1							
A	GB 1 309 402 A (MINNESOTA MINING AND MANUFACTURING COMPANY) 14 March 1973 * claims 1-17 *	1							
A	EP 0 244 839 A (AUSIMONT S.P.A.) 11 November 1987 * claims 1-8 *	1							
A	US 3 250 806 A (J. L. WARRELL) 10 May 1966 * claims 1-5 *	1							
A	EP 0 348 948 A (DAIKIN INDUSTRIES, LTD.) 3 January 1990 * column 3, line 6 - line 44; claims 1,2 *	1							
Y	EP 0 712 882 A (AUSIMONT S.P.A.) 22 May 1996 * the whole document *	1,8-15							
Y	EP 0 654 493 A (AUSIMONT S.P.A.) 24 May 1995 * page 3, line 9 - page 5, line 29; claims 1-12 *	1,8-15							
		-/-							
<p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 33%;">Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>10 July 1998</td> <td>Permentier, W</td> </tr> </table>				Place of search	Date of completion of the search	Examiner	THE HAGUE	10 July 1998	Permentier, W
Place of search	Date of completion of the search	Examiner							
THE HAGUE	10 July 1998	Permentier, W							
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document							
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document									



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 98 10 6099

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D, Y	US 3 847 978 A (D. SIANESI) 12 November 1974 * column 5, line 38 - column 6, line 56 * * column 6, line 27 - line 66; claims 1-25 * ----- A FR 2 148 230 A (MONTECATINI EDISON S.P.A.) 11 March 1973 * claims 1-5 * -----	1,8-15	
TECHNICAL FIELDS SEARCHED (Int.Cl.6)			
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search		Examiner
THE HAGUE	10 July 1998		Permentier, W
CATEGORY OF CITED DOCUMENTS			
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